

## (12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
14 October 2004 (14.10.2004)

PCT

(10) International Publication Number  
**WO 2004/087976 A1**

(51) International Patent Classification<sup>7</sup>: C22C 9/00

TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number:  
PCT/FI2004/000203

(22) International Filing Date: 2 April 2004 (02.04.2004)

(25) Filing Language: Finnish

(26) Publication Language: English

(30) Priority Data:  
20030508 3 April 2003 (03.04.2003) FI

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM; ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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- of inventorship (Rule 4.17(iv)) for US only

## Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

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(54) Title: OXYGEN-FREE COPPER ALLOY AND METHOD FOR ITS MANUFACTURE AND USE OF COPPER ALLOY

(57) Abstract: The invention relates to an oxygen-free copper alloy containing magnesium between 30 - 180 ppm, preferably 50 - 150 ppm in order to improve temperature resistance. The invention also relates to a method for the manufacture of the copper alloy and to the use of the copper alloy.

WO 2004/087976 A1

## **OXYGEN-FREE COPPER ALLOY AND METHOD FOR ITS MANUFACTURE AND USE OF COPPER ALLOY**

The invention relates to an oxygen-free copper alloy, in which there is alloyed material that increases temperature resistance. The alloy is particularly suited to be used in targets where both a good temperature resistance and a good electroconductivity is required of the alloy. The invention also relates to manufacturing the copper alloy and to the use of the copper alloy.

The oxygen content of the most generally used copper quality, so-called ETP copper (electrolytic tough pitch) is typically 200 – 400 ppm. Oxygen is naturally bound in copper in a regular manufacturing process. The oxygen content can also be kept on a desired level intentionally, because oxygen bounds harmful substances to less harmful oxides. The electroconductivity of copper is always the higher, the purer the copper is, and also the oxygen bound in copper reduces conductivity. The thermal conductivity of copper is proportional to its electroconductivity. Particularly for improving the electroconductivity, there is also manufactured so-called oxygen-free copper with an oxygen content not higher than 10 ppm. In the manufacturing of oxygen-free copper, oxygen is prevented from getting into contact with molten copper by using a protective, reducing layer on top of the melt (for example graphite), by using protective gas (for example nitrogen) or by using a vacuum.

The temperature resistance of oxygen-free copper has been improved by alloying silver in the copper, for example 0.02 – 0.3% of the alloy weight. Also magnesium has earlier been used as a microalloying ingredient, generally in very small contents. Other alloy ingredients are generally used at the same time. For example in the publications US-5118470, JP-A-62080241 and JP-A-03291340, there are described these types of alloys, which are used for producing connector wire employed in semiconductor technology. By melting, the wire is formed into drops that have a perfect ball shape. Said material also has a good tensile strength. Apart from other materials, magnesium is

suggested as an alloy ingredient also in the publication JP-A-63140052, for example. Here magnesium, with the content of 3 – 10 ppm, lowers the softening temperature of copper.

The object of the present invention is to eliminate some drawbacks of the prior art and to achieve an improved oxygen-free copper alloy. The essential features of the invention are enlisted in the claims.

According to the invention, over 30 ppm magnesium is alloyed in oxygen-free copper, when calculated of the alloy weight. Thus the temperature resistance is improved, while the electroconductivity and hence also thermal conductivity remain on a high level. The magnesium content of an oxygen-free copper alloy according to the invention is over 30 ppm, preferably over 50 ppm. The magnesium content is not higher than 180 ppm, preferably not higher than 150 ppm. The oxygen content of the alloy is not higher than 10 ppm, preferably not higher than 5 ppm, such as 1 – 3 ppm. The alloy is suited to be used particularly in products where there is required a good temperature resistance, and at the same time good electroconductivity or thermal conductivity. By means of the magnesium alloying according to the invention, the temperature resistance of copper is remarkably improved.

The temperature resistance of copper is generally expressed by the so-called half-softening temperature ( $T_{1/2}$ ). However, the half-softening temperature is remarkably dependent on the degree of deformation. In order to obtain comparable results, the half-softening temperature is generally defined with a degree of deformation of 40 % and 94 %.

The electroconductivity of copper is generally expressed by the so-called IACS-value (International Anneal Copper Standard). It expresses the electroconductivity in percentages of the electroconductivity of standard non-alloyed copper. The electroconductivity of an oxygen-free copper quality is at least 100 % IACS.

The half-softening temperatures of copper alloys according to the invention are at least of the same order as those of alloys containing 0.3 – 0.25% silver. With a 40% degree of deformation, the half-softening temperature is at least 340° C, preferably at least 380° C. With a 94% degree of deformation, the half-softening temperature is at least 300° C, preferably at least 335° C. Irrespective of alloying, the electroconductivity still remains on a high level (over 100 % IACS). Conductivity is preferably at least about 101 % IACS.

With contents over 180 ppm, the improving of the temperature resistance with respect to the magnesium quantity is essentially weakened. Also electroconductivity and castability are weakened. With magnesium contents of less than 30 ppm, essential improvements in the temperature resistance are virtually not achieved.

Here magnesium raises the recrystallization temperature of pure copper. Magnesium atoms are larger than copper atoms, wherefore the lattice structure is distorted, and tensions are created. Consequently the moving of dislocations becomes more difficult.

By means of the invention, there are reached savings in expenses in comparison with the use of silver, because magnesium is remarkably cheaper than silver, and it is needed in a remarkably smaller quantity than silver. Owing to the small quantity of alloy ingredient, also the alloying technique can be chosen more freely.

Magnesium alloyed copper can be manufactured by similar manufacturing techniques as other qualities of oxygen-free copper, for example in slab or rod casting, either as horizontal or vertical casting. In a suitable step of the process, for instance into the casting furnace, there is added a required amount of magnesium. Because magnesium is sensitive to react with oxygen, especial attention must be paid to protection from air. Also in devices that get into

contact with the melt, it is advantageous to use such oxide-free materials from which magnesium cannot bind oxygen. Casting is generally followed by thermal treatment and working. A typical route for manufacturing could be slab casting downwards and working by hot and cold casting. With these contents, magnesium can result in secondary grain structure, which must be taken into account when choosing the working temperature.

Phosphorus, silicon and sulfur can react with magnesium, thus weakening the improvement in temperature resistance. Therefore the total content of said impurities is preferably not higher than 10 ppm.

The copper according to the invention can be used in targets where a good temperature resistance is required. These are for instance commutators of electric motors, which contain several segments and the temperature of resins, which are used to fit segments together, will rise up higher than 200 °C. Further, the copper alloy of the invention can be used in substrate materials that are coated at high temperatures. For instance, solar panels are manufactured by high-temperature coating processes. One target is also the electrode tips used in welding, preferably in MIG welding, and flat bars and profiles used in generators, in which the copper alloy of the invention replaces the more expensive copper silver alloy.

In an alloy according to the invention, also other alloy ingredients can be used. These are particularly silver and phosphorus. It is well known that silver raises the half-softening temperature. The silver content is advantageously not higher than 500 ppm. Other possible alloy ingredients are for instance sulphur, tin, zinc, nickel, silicon and tellurium. Advantageously the content of these is not higher than 50 ppm. Also tin raises the half-softening temperature, but it is not as efficient as magnesium, and what is more, it lowers conductivity to a larger degree.

### Example

- There were manufactured magnesium alloyed oxygen-free copper alloys, in which there were alloyed magnesium 50, 100 and 150 ppm of the alloy weight.
- i The temperature resistance and electroconductivity of the alloys were compared with the temperature resistance and electroconductivity of known silver-copper alloys.

An annealed wire of 8 mm was manufactured of each material. The electroconductivity of the wire was measured. Thereafter the wires were drawn to the thickness of 6.2 mm (degree of deformation 40%) or 2 mm (degree of deformation 94%). The wires were annealed in a salt bath (1 h) within the range of 250 – 500° C. The results are given in the table below in which table for instance the marking Mg50ppm means the alloy of the invention, which contains 50 ppm magnesium, and the marking CuAg0.03 means the copper alloy of the prior art which contains 0.027 – 0.05 % by weight silver.

Alloy	Ag [% by weight]	Electroconductivity [%IACS]	T½ 40% [°C]	T½ 94% [°C]
CuAg0,03	0,027-0,05	100,88	340	295
CuAg0,1	0,085-0,12	100,77	360	325
CuAg0,2	0,20-0,25	101,10	380	340
Mg50ppm	-	101,95	363	310
Mg100ppm	-	101,40	379	335
Mg150ppm	-	100,84	386	340

It is apparent that with magnesium contents of 50 – 150 ppm, there are achieved properties that are at least as good as with silver contents of 0.027 – 0.25%.

## CLAIMS

1. An oxygen-free copper alloy containing oxygen not more than 10 ppm of the alloy weight, **characterized** in that the alloy contains, in order to improve temperature resistance, magnesium between 30 – 180 ppm of the alloy weight.
2. An alloy according to claim 1, **characterized** in that the alloy contains magnesium for over 50 ppm.
3. An alloy according to claim 1 or 2, **characterized** in that the alloy contains magnesium not more than 150 ppm.
4. An alloy according to any of the preceding claims, **characterized** in that the alloy contains oxygen not more than 5 ppm, preferably 1 – 3 ppm.
5. An alloy according to any of the preceding claims, **characterized** in that the half-softening temperature with a 40% degree of deformation is at least 340° C, preferably at least 380° C.
6. An alloy according to any of the preceding claims, **characterized** in that the half-softening temperature with a 94% degree of deformation is at least 300° C, preferably at least 335° C.
7. An alloy according to any of the preceding claims, **characterized** in that the electroconductivity is at least 100% IACS, preferably at least 101% IACS.
8. An alloy according to any of the preceding claims, **characterized** in that the alloy contains phosphorus, silicon and sulfur, their total content not surpassing 10 ppm.

9. A method for manufacturing oxygen-free copper alloy, said alloy containing oxygen not more than 10 ppm, **characterized** in that magnesium is alloyed in the alloy for over 30 ppm, but not more than 180 ppm of the alloy weight.

10. The use of copper manufactured according to any of the claims 1 – 8 or according to claim 9 in a product where there is required a good temperature resistance and a good electroconductivity or thermal conductivity.

11. The use of the claim 10 in commutators of electric motors.

12. The use of the claim 10 in a tip of a welding electrode.

13. The use of the claim 10 in generator profiles.

14. The use of the claim 10 in generator flat bars.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000203

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22C 9/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 016, no. 126 31 March 1992 (1992-03-31) & JP 3291340 A (MITSUBISHI MATERIALS CORP) 20 December 1991 (1991-12-20) abstract & JP-03-291340 A	1-7,9,10
A	--	8,11-14

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

26 August 2004

Date of mailing of the international search report

31-08-2004

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 2004/000203

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 199, no. 612, 26 December 1996 (1996-12-26) & JP 8209270 A (FURUKAWA ELECTRIC CO LTD:THE 13 August 1996 (1996-08-13) abstract & JP 08-209270 A	1-7,9,10
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

03/07/2004

International application No.

PCT/FI 2004/000203

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